Effects of solute-solvent attractive forces on hydrophobic correlations

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A theory is presented for the effect of slowly varying attractive forces on correlations between nonpolar solutes in dilute aqueous solution. We find that hydrophobic correlations are sensitive to relatively long range slowly varying interactions. Thus, it is possible to make qualitative changes in these correlations by introducing small changes in the attractive forces. Several model calculations are presented to illustrate these facts. The contributions of the Lennard-Jones attractive forces to the computer simulation results of Pangali, Rao, and Berne are calculated. For this case it is found that the potential of mean force between spherical nonpolar solutes is hardly affected by inclusion of attractive forces. However, the osmotic second virial coefficient is dominated by the contributions of the attractive forces. For spherical solutes which provide a reasonable model for the methane molecule, inclusion of attractive forces produces a qualitative change in the methane-methane potential of mean force. The connection between these effects of slowly varying attractive forces and the enthalpic part of B"{o}nn"{o}rn K"{a}h"{a}n is discussed.

I. INTRODUCTION

Much of the progress in the equilibrium theory of classical liquids over the last decade has been marked by an appreciation of the differing effects of rapidly varying (usually repulsive) forces, and slowly varying (usually attractive) forces. It is frequently found that slowly varying attractive forces play only a minor role in determining the structure of a dense liquid. Thus, it is usually a fruitful strategy for attacking new problems regarding the structure of dense liquids to begin by attempting to formulate a theory appropriate for the case in which slowly varying attractive forces are absent. If a successful theory for the repulsive force system can be constructed, then attractive forces can usually be included in a perturbative fashion.

An example of this tactic is found in our theory for hydrophobic solvation and hydrophobic interaction effects associated with apolar solutes in liquid water. The interactions between two apolar solutes, for example, methane molecules, include both attractive and repulsive forces. Our theory for the correlations associated with the solute molecules was designed for the case in which these correlations were determined primarily by solvent-solute repulsive forces. In this paper we consider the effects of attractive forces on hydrophobic correlations.

There are at least three motivations for this further development of our theory. The first is that since our theory for these hydrophobic effects was presented, computer simulation calculations have been performed on aqueous solutions of apolar solutes. These results present the possibility of reliably distinguishing even small changes in hydrophobic correlations due to attractive forces. More importantly, these calculations can provide an unambiguous test of the approximations we invoke to study hydrophobic phenomena. The most direct comparison can be made with the work of Pangali, Rao, and Berne (PRB). These workers calculated the potential of mean force between Lennard-Jones solutes dissolved in an extensively studied Hamiltonian model of liquid water, ST2 water. The results of PRB are in quantitative agreement with the results of our theory. If the effect of attractive forces on this potential of mean force are indeed small, then this close agreement can be taken as an experimental verification of our theoretical results.

A second motivation is that a large part of current thinking about hydrophobic effects is based on interpretation of measured thermodynamic properties of aqueous solutions. Thermodynamic properties of a dense liquid are typically more sensitive to inclusion of attractive forces than are structural properties. Thus a correct distinction between the roles of repulsive and attractive forces in these solutions seems necessary in order to reliably interpret thermodynamic measurements.

Finally, the role of attractive forces in liquid mixtures is somewhat different than in pure simple liquids. A consequence of this is that simple van der Waals theories have a different range of validity in liquid mixtures than in pure liquids. If there is a dissimilarity between solute-solute and solute-solvent attractive forces, it is possible that inclusion of attractive forces can produce a large change even in structural properties. One would like to understand exactly when such changes should be expected.

The reason that attractive forces may cause important structural changes in liquid mixtures is that in such systems there are a variety of structural changes which entail little change in repulsive force energy but large changes in attractive force energy. These structural changes have the nature of concentration fluctuations without total density fluctuations. An example of par-
ticular importance in this paper is depicted in Fig. 1. The shaded particles are solutes which we denote as species A. The solvent particles are species W. The two configurations have essentially the same probability if attractive forces are neglected. They also have essentially the same probability if the strength of the solute–solvent and solute–solvent attractive forces included are nearly equal. But if solute–solvent attractive forces are stronger than solute–solvent attractive forces for example, then one expects configuration (a) to be more likely than configuration (b).

If we consider the radial distribution at infinite dilution of A particles around a central A particle, \( g_{AA}(r) \), then we can form a simple estimate of the size of this attractive force effect in the following way. Note that

\[
\omega_{AA}(r) = -k_B T \ln g_{AA}(r; \rho_W, T)
\]

(1)

Here \( k_B \) is Boltzmann's constant, and \( \omega_{AA}(r) \) is the pair potential of mean force. Let

\[
\omega_{AA}^{(0)}(r) = -k_B T \ln g_{AA}^{(0)}(r)
\]

stand for the potential of mean force when solute–solvent and solute–solvent attractive forces are neglected. Assume the structure and thermodynamics of the pure solvent include all effects of the full solute–solvent interaction potential. Now focus on \( 5\omega_{AA}(r) = \omega_{AA}(r) - \omega_{AA}^{(0)}(r) \), and consider the configuration shown in Fig. 1(a).

Once the separation of the two A particles is fixed, further concentration fluctuations without total density fluctuations cannot contribute. Thus, to calculate the free energy of the fixed A–A pair, a mean field approximation should work. If \( \epsilon_{AA} \) measures the strength of the attractive A–W forces, and \( \epsilon_{AA} \) measures the strength of the A–A attractive forces, then for the two dimensional configuration of Fig. 1(a) we estimate the internal energy of the A–A pair to be \( -\epsilon_{AA} \). We arrive at this result because each A particle has roughly five near neighbors of species W, and the A particles are also near neighbors to each other. On the other hand, if \( r - r' \), we expect each A particle to have roughly six near neighbors. In this case, we would estimate the internal energy of the A–A pair to be \( -2\epsilon_{SW} \). On this basis we obtain

\[
5\omega_{AA}(r) = 2\epsilon_{SW} - \epsilon_{AA}
\]

(3)

for the configuration of Fig. 1(a). Note that \( 5\omega_{AA}(r) \) should include only the effect of attractive forces associated with the solute. If the solvent–solvent attractive forces were to be included in the perturbative approach the more symmetrical combination \( 2\epsilon_{SW} - \epsilon_{AA} - \epsilon_{SW} \) would appear. Here \( \epsilon_{SW} \) represents the strength of the attractive solvent–solvent interaction. In the present formulation, effects like the \( -\epsilon_{SW} \) are included in \( \omega_{AA}^{(0)}(r) \).

The theory we give in the next section allows quantitative implementation of these ideas. However, several conclusions may be drawn immediately from the physical picture we have described. The first point to note is that our argument has been limited to the case for which the solute molecules are at infinite dilution. This is the case for the hydrophobic correlation questions, and the only one we consider here. The results we derive are not directly applicable when the solutes are present at nonzero concentration. The second point is that this physical effect depends on a mismatch of attractive forces and an asymmetry in the environment of a particular A when a second A particle is nearby. On this basis we do not expect \( 5\omega_{AA}(r) \) to be large for pure fluids. We also do not expect the correlations between A particles and W particles to be sensitive to inclusion of attractive forces at infinite dilution of A. Thus, our physical picture will be correct if \( g_{AA}(r) = \exp(-\omega_{AA}(r)/k_B T) \) changes only slightly when attractive forces are included. However, whether \( g_{AA}(r) \) changes depends on the relative sizes of \( \epsilon_{AA} \) and \( \epsilon_{SW} \). The third point is that to implement these physical ideas we clearly need explicit information about three body A–A–W correlations. This is because to obtain the solvation energy of fixed A–A pair, we need to know the probability of finding W particles in particular regions around the two A particles.

Our theory for obtaining the necessary three body correlations is presented in the next section. We then show how these three body correlations can be used to calculate \( 5\omega_{AA}(r) \). Our approach can be compared with more standard theories for \( 5\omega_{AA}(r) \), e.g., the EXP approximation of Andersen, Chandler, and Weeks,23 in the regimes where both are applicable. We discuss this comparison in the next section also. In Sec. III, we present numerical results of calculations of \( 5\omega_{AA}(r) \) for several model systems. The first calculation is for the solutes studied by PRB. We find that for the attractive forces assumed in their work \( 5\omega_{AA}(r) \) is indeed pointwise

very small. Even though $\Delta u_{AA}(r)$ is pointwise very small, the osmotic second virial coefficient

$$B_2 = \frac{1}{2} \int dt \left[ \exp \left( -\frac{u_{AA}(r)}{kT} \right) - 1 \right]$$

(4)

is dramatically affected by inclusion of attractive forces. If we write

$$\partial B_2 = B_2 - B_2^{(0)}$$

(5)

and

$$B_2^{(0)} = \frac{1}{2} \int dt \left[ \exp \left( -\frac{u_{AA}(r)}{kT} \right) - 1 \right]$$

(6)

then $\partial B_2$ has the opposite sign to $B_2^{(0)}$, and the magnitude of $\partial B_2$ is larger than that of $B_2^{(0)}$. Consequently, $\partial B_2$ dominates $B_2^{(0)}$, and little can be learned about short range A-A correlations from interpretation of $B_2$ alone. This possibility has been suggested by us earlier, and should not be unexpected. The second calculation we present is for methanol solute. The strength of the attractive forces are chosen to make our theory consistent with the measured hydrophobic solvation properties of simple hydrocarbons. In this case, we find that $\Delta u_{AA}(r)$ is surprisingly large. This suggests that these attractive force effects may play a major role in hydrophobic phenomena of real systems. On this basis it is important that further computer simulations of aqueous solutions systematically attempt to identify the role of attractive forces in hydrophobic correlations. In the final section we discuss some similarities in form between the theory we present here and empirical Gurney potential representations of $\Delta u_{AA}(r)$. We also discuss the significance of these attractive force effects in understanding the behavior of the enthalpic part of Der-Naim's $\Delta A$.  

II. THEORY

To implement the physical arguments of the previous section, we utilize the exact expression

$$\Delta u_{AA}(R) = 2 \Delta u_{AA} - kT \ln y_{AA}(R)$$

(7)

for the excess chemical potential of an AA dimer rigidly separated by a distance $R$, $\Delta u_{AA}(R)$, when the A solute is at infinite dilution. The quantity $\Delta u_{AA}$ is the corresponding excess chemical potential at infinite dilution for A monomers, and $y_{AA}(R)$ is the indirect correlation function

$$y_{AA}(R) = e^{\Delta u_{AA}/kT} e_{2AA}(kT)$$

(8)

Here $\Delta u_{AA}(R)$ is the AA particle interaction potential energy and $e_{2AA}(kT)$ is the usual radial distribution function. Besides $\Delta u_{AA}(R)$, we also must consider the function $u_{AA}(R)$ which gives the interaction potential energy between A particles and solvent W particles. These potential energy functions must be separated into repulsive force $u_{AA}(R)$ and attractive force $u_{AA}(R)$ contributions

$$u_{AA}(R) = u_{AA}^{(0)}(R) + u_{AA}^{(1)}(R).$$

(9)

For the potential functions relevant to the present work, this separation is best accomplished by using the WCA prescription. We assume that $y_{AA}(R) = e^{\Delta u_{AA}/kT}$ is known; the superscript zero indicates properties evaluated with $\Delta u_{AA}(R) = 0$. This gives us

$$\Delta u_{AA}^{(0)}(R) = 2 \Delta u_{AA}^{(0)} - kT \ln y_{AA}(R).$$

(10)

Our corrections to $y_{AA}(R)$ due to $u_{AA}^{(1)}(R)$ are formulated by calculating the left-hand side of Eq. (7) to first order in $u_{AA}^{(1)}(R)$ (the high temperature approximation). We find

$$\ln y_{AA}(R) = a y_{AA}(R)$$

(11)

Of course, since the A particles are at infinite dilution $y_{AA}(R)$ does not depend on $u_{AA}(R)$. In this equation $\Delta u_{AA}^{(0)}$ is the radial distribution of solvent W particles in a shell of radius around a single spherical A particle; $p_{AA}^{(0)}(r)$ is the radial distribution of solvent W particles in a shell of radius around a spherical A particle when a second A particle is fixed a distance $R$ away. Thus, $\Delta u_{AA}^{(0)}(r)$ gives the A-W correlations when the A particle is fixed in a rigid diatomic molecule of bond length $R$.

The chief obstacle to use of Eq. (11) is the evaluation of $\Delta u_{AA}^{(0)}(r)$, which is $\Delta u_{AA}^{(1)}(r)$ obviously contains explicit information about three body AAW correlation. We have emphasized elsewhere9 that the use of standard superposition approximations for the calculation to qualitatively incorrect results. This is also the case here. If we use the superposition approximation, we obtain

$$\Delta u_{AA}^{(0)}(r) = s_{AA}^{(0)}(r) \frac{1}{2\pi R} \int_{r-R}^{r+R} dx \; s_{AA}^{(0)}(x),$$

(12)

Then Eq. (11) gives, for $R = 0$,

$$\ln y_{AA}(0) = \ln y_{AA}(0) = -2 \int_{-R}^{R} dx \; s_{AA}^{(0)}(x) - 11 \Delta u_{AA}^{(1)}(0).$$

(13)

However, the correct result is

$$\Delta u_{AA}^{(0)}(r) = s_{AA}^{(0)}(r),$$

$$\ln y_{AA}(0) = \ln y_{AA}(0).$$

This follows from the fact that when $R = 0$, the diatomic molecule is spherical.

Aside from its use in Eq. (11), the correlation function $s_{AA}^{(0)}(r)$ is of interest because it describes the solvation of an AA molecule in the solvent W. Consideration of $s_{AA}^{(0)}(r)$, which relies on the same approximations as our theory for $s_{AA}^{(0)}(r)$. The previous paper11 presented and discussed numerical applications of our theory for $s_{AA}^{(0)}(r)$ for simple nonspherical hydrocarbon solute in aqueous solution. Such a theory for $s_{AA}^{(0)}(r)$ allows immediate use of Eq. (11) to calculate $\ln y_{AA}(R)$ for $y_{AA}(R)$.
some existing theories for the effects of attractive forces in simple liquids.

We first note that Eq. (11) predicts

\[ \delta \sigma_{AA}(r) = \sigma^{(0)}_{AA}(r) \exp \left[ -\frac{\delta \sigma_{AA}(r)}{k_B T} \right] , \]

\[ \delta \sigma_{AA}(r) = 2 \delta \| \int dr_r \left[ \sigma^{(0)}_{AA}(r) - \frac{\delta \sigma_{AA}(r)}{k_B T} \right] \right] . \]

Equation (15) is exact in the limit of low \( \rho \). Because of the form of Eq. (15) the present theory is most easily compared with the EXP approximation of Andersen, Chandler, and Weeks. This approximation is

\[ \delta \sigma_{AA}(r) = \sigma^{(0)}_{AA}(r) \exp[C_{AA}(r)] , \]

where \( C_{AA}(r) \) is given (for the present circumstance), by the solution of the integral equation

\[ C_{AA}(r) = \theta_{AA}(r) + \rho_B \phi_{AA}(r), \]

\[ C_{AA}(r) = \theta_{AA}(r) + \rho_B \phi_{AA}(r) \left[ C_{AA}(r) + 2 \sigma^{(0)}_{AA}(r) \right] , \]

\[ \theta_{AA}(r) = -\frac{\sigma^{(0)}_{AA}(r)}{k_B T} , \quad r > a_{AA} , \]

\[ C_{AA}(r) = 0 , \quad r < a_{AA} . \]

The asterisks indicate convolution integrals (for notation see the previous paper). The EXP approximation also gives the correct limiting behavior for low \( \rho \). This approximation is usually considered to be correct when the integrated magnitude of \( C_{AA}(r) \) is small. In that case, the corrections to \( \sigma^{(0)}_{AA}(r) \) are small. However, our derivation of the new result, Eq. (11), makes it clear that the mean field approximation can be quantitatively correct even though the magnitude of \( \ln \left[ \delta \sigma_{AA}(r)/\sigma^{(0)}_{AA}(r) \right] \) is very large. In order to be accurate, the mean field theory requires that \( \ln \left[ \delta \sigma_{AA}(r)/\sigma^{(0)}_{AA}(r) \right] \) be small. The new theory will be correct if this condition is met because it was derived by a systematic high temperature approximation.

Finally, we point out that although Eq. (11) assumes that \( \ln \left[ \delta \sigma_{AA}(r)/\sigma^{(0)}_{AA}(r) \right] \) is small, we have not presented a theory for \( \delta \sigma_{AA}(r) \). If \( \delta \sigma_{AA}(r) \) is in fact only slightly changed by inclusion of attractive forces, then one expects that the standard theories, e.g., the EXP approximation, will correctly predict \( \delta \sigma_{AA}(r)/\sigma^{(0)}_{AA}(r) \). The calculations reported below we use the EXP approxi-

![FIG. 2.](image1.png) Variation of dimensionless solvation energy of a rigid A-A dimer with bond length \( r \) (see Eq. [23]). The A-W distance of closest approach is taken to be 3.43 Å appropriate to the PRB simulation (Ref. 5). The temperature is 25 °C.

![FIG. 3.](image2.png) Contribution due to attractive forces to A-A radial distribution for the system studied by PRB (Ref. 5). The dashed line is the result of EXP approximation, Eq. (17), for \( \delta \sigma_{AA}(r) \) of Eq. (22); the lower solid line is the corresponding result of our mean field approximation. The temperature is 25 °C.

**III. RESULTS**

A. Effects of attractions in system studies by PRE (Ref. 6)

Pangali, Rao, and Bernier have used computer simulation techniques to calculate \( \delta \sigma_{AA}(r) \) for Lennard-Jones-type solutes in ST2 water. They took the \( u_{AA}(r) \) to have the form

\[ u_{AA}(r) = \frac{4}{3} \sigma^{(0)}_{AA}(r) \left[ (\sigma_{AA}(r)/r)^3 - (\sigma_{AA}(r)/r)^6 \right] , \]

with

\[ \sigma_{AA} = 4.12 \text{ Å}, \quad \sigma_{AA}/k_B = 170.1 \text{ K}, \]

\[ \sigma_{AW} = 3.43 \text{ Å}, \quad \sigma_{AW}/k_B = 77.82 \text{ K} . \]

We have used Eq. (11), with

\[ \delta \sigma_{AA}(r) = \begin{cases} 0, & r < a_{AA} \\ \frac{-\delta \sigma_{AA}(r)}{k_B T}, & r > a_{AA} \end{cases} \]

\[ \delta \sigma_{AA}(r) = \begin{cases} -\delta \sigma_{AA}(r), & r < 2^{1/3} \sigma_{AA} \\ u_{AA}(r), & r > 2^{1/3} \sigma_{AA} \end{cases} \]

\[ u_{AA}(r) = \begin{cases} 0, & r < \sigma_{AW} \\ \frac{4}{3} \sigma^{(0)}_{AA}(r) \left[ (\sigma_{AA}(r)/r)^3 - (\sigma_{AA}(r)/r)^6 \right] , & r > \sigma_{AW} \end{cases} \]

\[ \text{to calculate the change in } \delta \sigma_{AA}(r) \text{ due to attractive forces} \]

\[ \text{and } \delta \sigma_{AA}(r) = \frac{\delta \sigma_{AA}(r)}{1 - e^{\phi_{AA}(r)/k_B T}} . \]

Of course, the \( \sigma_{AA}(r) \) for smooth repulsive \( \sigma^{(0)}_{AA}(r) \) can be obtained from our results using the hard sphere interaction, Eq. (20), in the standard way. The AA pair solvation energy

\[ \left( \frac{u^{(0)}_{AA}}{\sigma_{AA}} \right) = \frac{2}{3} \rho \int dr_r \left[ \sigma^{(0)}_{AA}(r) / \sigma_{AA} \right] \]

is shown in Fig. 2. This quantity yields the mean field prediction for \( \delta \sigma_{AA}(r) \) shown in Fig. 3. Also shown are
\( \delta g_{AA}(r) \) from the EXP approximation for comparison. These predictions for \( \delta g_{AA} \) are small compared to \( g_{AA}(r) \), and except very near contact, \( r = 4.12 \, \text{Å} \), the mean field and EXP theories are in good agreement. Note that if the softness of the real core repulsive forces used by PRB are accounted for, then the absolute magnitude of these \( \delta g_{AA}(r) \)'s near contact will be further reduced by about 50%. In any case, the corrections to \( g_{AA}(r) \) due to the attractive solute–solvent forces included in the PRB simulation are never more than \( 10\% \). It appears that the uncertainties involved in the simulation techniques, due to statistics and perhaps other sources, \(^1\) are at least this large. Thus, the PRB result does indeed provide experimental support for the detailed results of our theory.

Since the attractive forces play such a small role in \( g_{AA}(r) \) it is of special interest here to consider what effect they have on \( B_2 \). In order to use our mean field approximation for this calculation care must be taken in order to treat the large \( r \) behavior accurately. This is because for large \( r \) the two quantities within the integral in Eq. (15) are nearly cancelling and direct numerical subtraction causes a loss of numerical precision. However, it is easy to see that for large \( r \)

\[
\begin{align*}
\delta g_{AA}(r) &= \int dr' \left( g_{AA}^{(0)}(r') - g_{AA}^{(1)}(r') \right) \left( n_A(r) - n_A^{(1)}(r) \right) \\
&= \int dr' \left( g_{AA}^{(0)}(r') \delta n_A(r') + g_{AA}^{(1)}(r') \delta n_A^{(1)}(r') \right).
\end{align*}
\]  

This is obtained by noting that the superposition approximation, Eq. (2), becomes exact for large \( r \) for the solvents studied by PRB we use the mean field approximation and find

\[
B_2 = \frac{E}{2} \int \delta g_{AA}(r) = -28 \, \text{Å}.
\]

at 25 °C. Since \(^1\)

\[
B_2 = 14 \, \text{Å}.
\]

we see that attractive forces provide the dominant contribution to \( B_2 \). The most important contributions to \( \delta B_2 \) come at large separations, \( r \geq 4 \, \text{Å} \), where \( \delta g_{AA}(r) \) is less than about 3% of \( g_{AA}(r) \) but persistently negative. We conclude that without a reliable theoretical method to separate short range effects on \( g_{AA}(r) \) from long range slowly varying mean field effects, interpretation of \( B_2 \) alone can be misleading.

We can show how these mean field contributions to \( B_2 \) are expected to vary as the temperature is changed. When the calculation above is repeated for 35 °C we find

\[
B_2 = -26 \, \text{Å}.
\]

Thus for this set of interactions we find that the contribution \( B_2 \) has less attractive character at the higher temperature. For the present situation this is a consequence of the fact that our mean field result is a high temperature approximation. The influence of attractive forces therefore is diminished as the temperature is raised. Since here we find that \( \delta B_2 \) is negative (attractive), raising the temperature decreases the attractive character of this contribution. However, the situation in which \( \delta B_2 \) is positive can also occur, and then raising the temperature will cause \( B_2 \) to appear to have more attractive character.

Since the values of \( B_2 \) are found to be sensitive to features of the assumed interactions, comparison with measured values of \( B_2 \) for real systems with incompletely known interactions does not seem very revealing. It seems likely that three-body and higher order contributions to the interaction potential should be examined. Also, the influence of orientational correlations must be included in any correct description of \( B_2 \) for nonspherical molecules. \(^10\)

In closing this section, it is convenient to emphasize that the theory for the effects of attractive forces is nontrivial even for the circumstances studied by PRB. This can be exemplified by considering the theory obtained by adopting the asymptotic result, Eq. (24), for all \( r \). \( A \) priori it is hard to argue that this theory should be better or worse than, for example, the EXP approximation. However, these two theories give surprisingly different results for \( g_{AA}(r) \) near contact. \( g_{AA}(r) \) is found to be the same, but each of these theories predicts a different sign. As mentioned earlier, the EXP approximation result is fairly close to that of our mean field approximation. In view of this sensitivity, the fact that our mean field approximation is the first term in a systematic high temperature expansion is a great virtue of our approach.

B. Effects of attractive forces on methane–methane correlations

Our theory provides a good description of the solvation of methane and small hydrocarbons \(^2\) if we use potentials of the Lennard–Jones form, Eqs. (20) and (21), and

\[
\begin{align*}
\sigma_{AA} &= 3.7 \, \text{Å} , \quad \epsilon_{AA}/k_B = 148 \, \text{K} , \\
\sigma_{AW} &= 3.2 \, \text{Å} , \quad \epsilon_{AW}/k_B = 168 \, \text{K}.
\end{align*}
\]

Before determining the effects of attractive forces on methane–methane correlations, we first inquire whether \( g_{AA}(r) \) is appreciably changed by inclusion of attractive forces. Figure 4 shows the results obtained by adopting the EXP approximation for \( g_{AA}(r) \). Near the maximum \( g_{AA}(r) \) is increased by about 10%. This is a reasonably small change. Thus, we use Eq. (23) to calculate \( \langle n_A^{(0)}/n_A \rangle \) (Fig. 5) and the mean field theory for \( g_{AA}(r) \) (Fig. 6), at \( T = 35 \, \text{°C} \). Since \( g_{AA}(r) \) is \( \approx 2.72 \) here, \(^1\) inclusion of attractive forces produces a 40% change, and \( g_{AA}(r) \) looks qualitatively different from \( g_{AA}(r) \). The change in \( B_2 \) due to attractive forces is found to be \( 0.13 \, \text{Å} \). (Remarkably, the prediction of the EXP approximation in these circumstances is qualitatively similar to that of our mean field theory.) It is easy to interpret these results on physical grounds. The solvation energy of the rigid AA pair is lower when their separation is increased for \( r > 3 \, \text{Å} \). Since \( \epsilon_{AW} > \epsilon_{AA} \) for this case, the solvation energy dominates the direct AA interaction, and the first peak of \( g_{AA}(r) \) is greatly reduced. To show the importance of this change most clearly, Fig. 7 shows the potential of mean field between two methane molecules when the
The sensitivity to attractive forces which we find in $\varepsilon_{\text{AA}}(r)$ indicates that it is important to pursue further computer simulation calculations comparable to those of PHB for systems with larger $\varepsilon_{\text{AA}}$, and possible even more general solute–solute interactions.

Finally, we note that some of the thermodynamic solvation properties of nonspherical hydrocarbons in water depend sensitively upon the cavity distribution $\varepsilon_{\text{AA}}(r)$. Important examples of such properties are Ben-Naim's $5A_{\text{ex}}^2$, and the free energy of transfer of hydrocarbons between nonassociated solvents and water. These properties are also sensitive to attractive forces, but we have already incorporated an estimate of the effects of attractive forces in our previous work. This estimate was formed by consideration of pure simple liquids, in which case $\varepsilon_{\text{AA}}(r) = 0$. For a pure system, $W = A$. Together with Eq. (15) this yields

$$2\sigma_{\text{AA}} \int dr \left[ \varepsilon_{\text{AA}}(r) - \varepsilon_{\text{AA}}(r) \right] a_{\text{AA}}(r) = \varepsilon_{\text{AA}}, \quad r \leq \sigma_{\text{AA}}. \quad (28)$$

Our previous results used this estimate when evaluating $y_{\text{AA}}(r), \quad r \leq \sigma_{\text{AA}}$. With the more detailed theory for attractive forces presented here we can do better. As an example we consider Ben-Naim's $5A_{\text{ex}}^2$ (Refs. 1 and 17) for ethane

$$5A_{\text{ex}}^2 = 2\varepsilon_{\text{AA}}(r) - 2A_{\text{ex}}.$$ 

$$= -8\pi \frac{\varepsilon_{\text{AA}}(r) \varepsilon_{\text{Me}}}{r \varepsilon_{\text{Me}}} (r = 1.54 \text{ Å})$$

$$= -8\pi \frac{A_{\text{ex}}}{r \varepsilon_{\text{Me}}} (r = 1.54 \text{ Å})$$

$$+ 2\sigma_{\text{Me}} \int dr \left[ \varepsilon_{\text{Me}}^{\text{ex}}(r) - \varepsilon_{\text{Me}}^{\text{ex}}(r) \right] a_{\text{Me}}(r). \quad (27)$$

Here $E_{\text{ex}}$ stands for ethane, and the third line above adopts our mean field approximation. The value of the integral in Eq. (27) can be read from Fig. 5. It is $1.2\sigma_{\text{Me}}$. With the interactions of Eq. (25), we find $5A_{\text{ex}}^2 = -2.27$ kcal/mole. Our previous estimate, Eq. (26), gives $5A_{\text{ex}}^2 = -2.41$ kcal/mole, and the experimental result is $-2.18$ kcal/mole. Thus the theoretical result is changed by about 4%, and the agreement between theory and experiment is improved. In view of the slight change, the more complicated calculations for larger hydro-
carbon particles are necessary. However, we point out that the comparison presented previously of theory with experiment for the transfer free energies of m-alkanes is incorrect. The results of the experiments are referred to a different standard state than those of the theory. To make a correct comparison, $k_B T \ln \left[ \frac{p_{mc} / \rho_s}{p_b} \right]$ must be added to the experimental data. Here, $p_{mc}$ is the number of density of the hydrocarbon solvent. For the normal alkane transfer considered in Ref. 1, this factor is 2.00. $T$, when $p_{mc}$ is taken to be the density of n-hexane at $T = 35^\circ C$. Figure 8 shows the correct comparison. The theoretical results are from Ref. 1 unchanged. The agreement is much improved.

IV. DISCUSSION

The theory and calculations presented above indicate that correlations between nonpolar molecules in liquid water depend sensitively on slowly varying interactions between solute and solvent and between solute molecules. To describe these effects we have presented a systematic theory with a clear regime of validity. In the mean field theory we developed, the quantity

$$5 \nu_{AA}(r) = \nu_{AA}(r) = 2 \nu_{AA}(r) \left[ \delta \left( \rho_{AA}(r) \right) \right] - \rho_{AA}(r) \delta \left( \rho_{AA}(r) \right)$$  

represents a deficiency of the solvation energy of the AA pair due to the proximity of each A particle to the other. This idea of a solvation deficiency is frequently used to motivate the introduction of an empirical Gurney potential representation of $\nu_{AA}(r)$. The empirical Gurney potentials can be used to categorize some of the thermodynamic data on properties of aqueous solutions. The results of this paper indicate that Eq. (28) is likely to be good first approximation to $\nu_{AA}(r)$ for aqueous solutions of nonpolar spherical A particles. Thus, for cases in which we have good experimental data and accurate knowledge of $n_{AA}(r)$ and $\nu_{AA}(r)$, it will be worthwhile to extend the additional effort required to implement Eq. (28) accurately. Useful and nontrivial information can be obtained even from evaluation of the integral, Eq. (28), by assuming the $\rho_{AA}(r)$ to have their low $\rho_b$ forms. For those circumstances the less empirical analysis can be expected to reveal interesting microscopic features of the solvation of the solutes. For example, Ben-Naim's theory of the enthalpic contribution to $\delta H_{TE}^f$ is found to be positive; that is

$$\delta H_{TE}^f = \frac{5 \rho_{AA}(r)}{2} \delta \left( \rho_{AA}(r) \right) \left( r = 1.54 \text{ Å} \right) > 0$$

On this basis Ben-Naim concludes that the clustering tendency for methane molecules in solution increases as the temperature increases. Our mean field result can be used to examine this conclusion in more detail. When Eq. (11) is used in Eq. (29) we obtain

$$\delta H_{TE}^f \left( r = 1.54 \text{ Å} \right) = \frac{5 \rho_{AA}(r)}{2} \delta \left( \rho_{AA}(r) \right) \left( r = 1.54 \text{ Å} \right)$$

According to our theory, the first term on the right-hand side of Eq. (30) is negative but very small, and the last term is positive but also small. The second term on the right-hand side of Eq. (30) is much larger than the other two and it is positive. For the interaction potentials we consider here, the value of this second term is 1.30 $\text{cal}$. Thus detailed study of this quantity [see also Eq. (28)] can be expected to clarify the observed behavior of Ben-Naim's $\delta H_{TE}^f$. However, knowledge of the relevant interaction potential energies, and the extent to which they can be pairwise decomposed is likely to be a major limitation on the realistic application of these results.

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